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PRODUCTION OF PITCH-BASED CARBON FIBER

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PRODUCTION OF PITCH-BASED CARBON FIBER

[Picchikei tan'sosen'i seizoh houhoh]

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Claim

Production method of a pitch-based carbon fiber characterized by the fact that hot-melt spinning is done for a mixture of a coal-based mesophase pitch and a petroleum-based mesophase followed by insolubilization and firing.

Detailed description of the invention

Industrial application filed

The present invention pertains to the production of a pitch-based carbon fiber. More precisely, the invention pertains to the production of a pitch-based carbon fiber useful for shortening of insolubilization (oxidation reaction) time of mesophase pitch fiber and preventing cracking in the cross-section of the fiber.

Prior art

A mesophase pitch-based carbon fiber is produced via a process that comprises production of the mesophase raw material, spinning, insolubilization, and firing. In general, pitch is spun under a low viscous state of 100 to 300 poise, discharged from a nozzle, and rapidly formed into a fine fiber. However, unlike standard polymer compounds, the temperature dependency of the viscosity of pitch is very high, and is strongly influenced by changes in viscosity of the pitch used as a spinning raw material despite careful temperature control provided for the spinning atmosphere, and fiber rupturing is very likely to occur.

Therefore, in order to achieve stable hot-melt spinning of an optically anisotropic mesophase pitch, it is necessary to employ a spinning temperature, nozzle, and shape of flow passage that make spinning a stable fiber possible. In this case, in general, the method described in Japanese Kokai Patent Application No. Sho 62-85031 where a spinning temperature that is as low as possible is used to prevent foaming, the diameter of the hole on the nozzle is reduced for stable spinning, and increasing the length of hole is desirable, but the shear applied to the pitch is increased; thus, a carbon fiber having a cross-section with a radial structure is formed, cracking is likely to occur, and properties are degraded.

On the other hand, as a means to avoid formation of a radial structure, the spinning temperature is increased, but the above-mentioned foaming problem occurs.

And furthermore, an insolubilization treatment is necessary for the pitch fiber before firing, but the insolubilization reaction rate at low temperatures is very low at the time of insolubilization that consists of heating with an oxidization gas; thus, in general, a reaction process where the temperature is increased with progress of the insolubilization is used. In this case, it is necessary to increase the temperature to a range that does not exceed the softening point accompanied by the insolubilization reaction.

When insolubilization is not provided, taking the aforementioned point into account, localized heat reserve occurs when bundled, and adhesion and fusion among adjacent fibers is likely to occur even when temperature control is provided at the time of the insolubilization process since the oxidation reaction, which is the insolubilization reaction for pitch, is an exothermic reaction. The aforementioned adhesion and fusion of fibers become surface defects and properties of the fiber are sharply reduced.

Because of the above-mentioned properties, completion of the insolubilization process requires a very slow temperature increase rate despite a higher reaction rate at higher temperatures, as a consequence, the treatment time required for insolubilization is extended.

And furthermore, flaws formed at the time of the insolubilization treatment become a major cause of degradation of the properties of the carbon fiber, and internal distortion caused by

escaping of detached components at the time of firing and shrinkage accompanied with formation of the structure based on development of the cross-section of the carbon [occur] especially at and near the surface.

In other words, due to properties of the raw material of the mesophase pitch, stable production of a carbon fiber based on shortening of insolubilization process by means of oxidation and prevention of cracks in the cross-section of the fiber is very difficult to achieve.

Problems to be solved by the invention

The purpose of the present invention to provide a method of producing a carbon fiber with a reduced insolubilization treatment time while preventing cracks forming in the cross-section of the fiber using a spinning method that takes advantages of the properties of mesophase pitch.

Means to solve the problem

The present invention pertains to the production of a pitch-based carbon fiber characterized by the fact that hot-melt spinning is done for a mixture of a coal-based mesophase pitch and a petroleum-based mesophase pitch followed by insolubilization and firing.

The present invention is explained in further detail below.

For the spinning mesophase pitch raw material used in the present invention, those having a softening point of 220 to 300°C, toluene insoluble parts (TI) of at least 70 wt%, and optical anisotropy of at least 80 vol% are desirable.

Furthermore, when a specific ratio of coal type mesophase pitch is mixed with a petroleum type mesophase pitch, an increase in the insolubilization rate of the petroleum type pitch can be achieved.

The mixing ratio of the coal type/petroleum type mesophase pitch is preferably in the range of 5/95 to 95/5.

For the spinning method used for mesophase pitch, in general, hot-melt spinning is used.

The relationship between the insolubilization process temperature and the oxygen content in the insolubilized fiber used as a rule of thumb for the oxidation reaction rate is shown in Figure 1.

As shown in Figure 1, an increase in insolubilization rate can be achieved when coal type mesophase pitch is mixed with a petroleum type mesophase pitch.

Furthermore, an insolubilized fiber with an oxygen content of 6% or less undergoes fusing with monofibers upon firing.

The cross-section view of carbon fiber is shown in Figure 2(a) to Figure 2(e).

When a coal type pitch alone is used, the fiber takes on a radial structure and cracking is observed in a majority of the fibers as shown in Figure 2(a).

When a petroleum type pitch alone is used, the fiber takes on a radial structure and cracking is observed in a majority of the fibers as shown in Figure 2(b).

On the other hand, when the petroleum type mesophase pitch and coal type mesophase pitch are blended as in the case of the present invention, basically, a two layer structure is formed as shown in Figure 2(c) (petroleum type mesophase pitch/coal type mesophase pitch 80/20), Figure 2(d) (50/50) and Figure 2(e) (20/80), and carbon fibers without cracking can be produced.

In other words, when a petroleum type mesophase pitch is added to a coal type mesophase pitch, an increase in the insolubilization rate and prevention of cracking can be achieved, and increase in the insolubilization rate within a specific range can be achieved.

The above-mentioned effect can be achieved for the first time when blending is done after forming into the mesophase pitch, and the effect of the present invention cannot be achieved when mesophase treatment is provided after mixing in a heavy oil state as described in the method of Japanese Kokai Patent Application No. Sho 59-116421.

For the blending method used for petroleum type mesophase pitch and coal type mesophase pitch, a method where pulverization mixing or hot-melt mixing of the mesophase pitches is performed can be used. A variety of kneading devices can be used when hot-melt mixing is used. Furthermore, it is desirable when a stationary type kneading device is used when kneading is performed inside the spinner or when the mixed mesophase pitch is supplied to a spinner.

The spinning method used is not especially limited, and hot-melt spinning, dry spinning, wet spinning, or wet and dry spinning may be used. In this case, hot-melt spinning is especially desirable.

For the insolubilization treatment, for example, a method where oxidation is done in the presence of oxygen, usually in air, at a temperature of 250 to 420°C can be used. Furthermore, a method where an oxidizing gas such as ozone, nitrogen oxide, and sulfur oxide is used in place of oxygen, or a method where an oxidizing liquid such as nitric acid, hydrogen peroxide solution, or potassium permanganate can be used as well.

For the carbonization treatment, a method where heating is done to 800 to 1700°C in an inert gas atmosphere or in a vacuum can be mentioned, and for graphitization treatment, a method where a heat-treatment is applied at 1700°C or above in an inert atmosphere can be mentioned.

The present invention is explained in further detail with working examples below. Furthermore, the measurement methods used in the working examples are explained below.

Optical anisotropy

The sample was wrapped in an epoxy resin and polishing is done in the usual manner. The value was obtained from the area ratio of the isotropic portion to the anisotropic portion when the polished surface is examined under reflected polarized light using an ORTHOPLAN microscope of Leitz Co. Ten measurements were made and the mean value was used.

Elemental analysis

A CHN Coda [transliteration] Model MT-3 of Yanagimoto Manufacturer was used and measurements were made under measurement conditions where a sample decomposition furnace temperature of 900 to 950°C was used, oxidation furnace temperature of 850°C, reducing furnace temperature of 550°C and helium flow rate of 180 mL/min. The measurement was made two times and the mean value is shown.

Measurement of tenacity

The measurement was made according to the method specified in JIS-R-7601. The diameter of the fiber was measured in the area adjacent to the tenacity measurement area using a scanning electron microscope. Furthermore, the area of the decomposed fiber was obtained from the cross-section in the micrograph.

Working examples

A coal type mesophase pitch (softening point 245°C, TI 83 wt%, and anisotropy 85 vol%) and a petroleum type mesophase pitch (softening point 250°C, TI 79 wt%, and anisotropy 98 vol%) were used, and spinning was done with different mixing ratios of the pitch. Discharge was from a nozzle with a nozzle opening diameter of 0.3 mm and hole length of 0.3 mm at different spinning temperatures and take-up was at a rate of 600 m/min to produce a pitch fiber with a diameter of 10 μm.

Subsequently, the temperature was increased from 50°C to a specific temperature in air at a rate of 0.5°C/min to produce an insolubilized fiber. In each case, the maximum weight increase was observed at around 330°C to 360°C, and it appears that the insolubilization is completed in the aforementioned temperature range. Firing of the resulting insolubilized fiber was performed in nitrogen at a temperature of 1500°C and 2500°C to produce carbonized fiber and graphitized fiber.

The oxygen content of the insolubilized fiber and properties of the carbonized fiber and graphitized fiber are shown in Table 1.

In comparison to Test Nos. 1 to 4 and Test Nos. 12 to 16 of comparative examples, Test Nos. 5 to 11, which are examples of the present invention, exhibit higher insolubilization rates,

and an absence of rupturing of the carbonized fibers, and possess the excellent properties of both the carbonized fiber and graphitized fiber.

Table I

①実験No	②ピッチ ⑤石炭系/石油系	⑥紡糸温度 (℃)	⑦不融化温度 (℃)	⑧酸素含有率 (%)	③炭化糸 強度 (Kg/mm2) ⑨	③炭化糸 弾性率 (ton/mm2) ⑩	④黒鉛化糸 強度 (Kg/mm2) ⑨	④黒鉛化糸 弾性率 (ton/mm2) ⑩	炭化糸割れ ⑪	
1	10/0	330	300	9.2	150	12	110	35	有	
2	10/0	330	330	11.1	160	14	100	40	有	⑫
3	10/0	330	360	12.3	160	14	110	35	有	
4	10/0	350	330	11.3	150	14	100	45	有	
5	8/2	330	330	13.4	180	14	280	55	無	
6	5/5	330	330	16.8	170	14	270	50	無	
7	2/8	330	300	17.9	180	13	280	55	無	
8	2/8	330	330	22.0	200	15	290	55	無	⑬
9	2/8	330	360	25.1	190	14	270	50	無	
10	2/8	320	330	22.1	200	14	280	50	無	
11	2/8	350	330	21.7	210	16	300	60	無	
12	0/10	330	300	15.4	160	11	100	40	有	
13	0/10	330	330	19.3	170	12	120	40	有	
14	0/10	330	360	23.0	170	12	100	45	有	⑪
15	0/10	320	330	18.9	150	11	100	30	有	
16	0/10	350	330	19.1	160	14	110	35	有	

Key:

1	Test No.
2	Pitch
3	Carbonized fiber
4	Graphitized fiber
5	Coal type/petroleum type
6	Spinning temperature (°C)
7	Insolubilization temperature (°C)
8	Oxygen content (%)
9	Strength (kg/mm^2)
10	Modulus (ton/mm^2)
11	Rupture of carbonized fiber
12	Yes
13	No

Effect of the invention

In the present invention, a coal type mesophase pitch and petroleum type mesophase pitch are mixed and used; thus, oxidation is promoted compared to the case where the mesophase pitch is used independently, and production of a superior carbon fiber with an absence of cracking in the cross-section is made possible.

<u>Brief description of the figures</u>

Figure 1 shows the relationship between the insolubilization treatment temperature and the oxygen content in the insolubilized fiber used as a rule of thumb of the oxidation reaction rate, and Figure 2(a) is a micrograph of the cross-sectional view of carbon fiber made of a coal type mesophase pitch alone, Figure 2(b) is a micrograph of the cross-section view of carbon fiber made of petroleum type mesophase pitch alone, Figure 2(c) to Figure 2(e) are micrographs of the cross-sectional views of carbon fibers produced by mixing of coal type mesophase pitch/petroleum type mesophase pitch of the present invention (Figure 2(c) 80/20), (Figure 2(d) 50/50) and (Figure 2(e) 20/80).

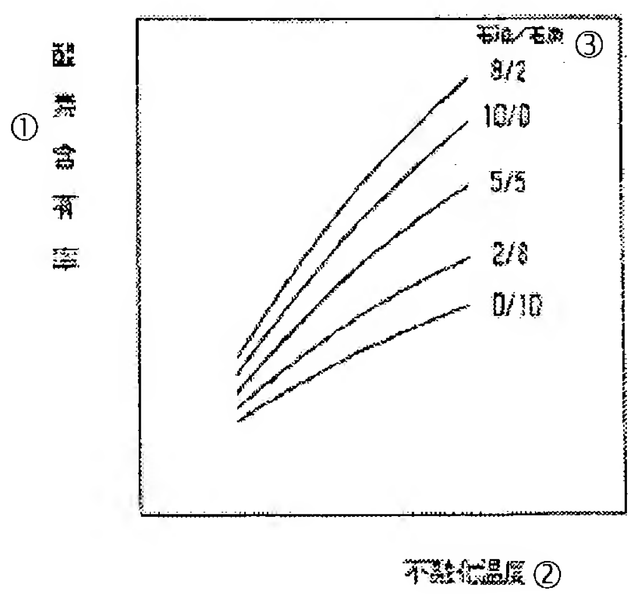

Figure 1

Key: 1 Oxygen content
2 Insolubilization temperature
3 Petroleum/carbon

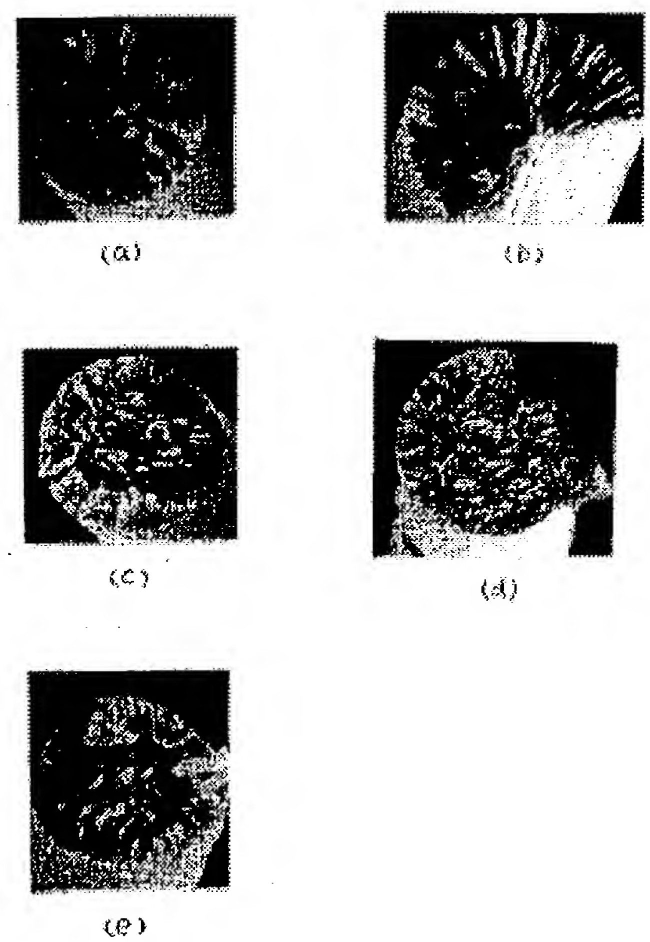

Figure 2